



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup>:</b> <b>C11D 3/39, 3/00</b>	<b>A2</b>	<b>(11) International Publication Number:</b> <b>WO 98/23717</b> <b>(43) International Publication Date:</b> 4 June 1998 (04.06.98)
<b>(21) International Application Number:</b> PCT/EP97/06164 <b>(22) International Filing Date:</b> 31 October 1997 (31.10.97)  <b>(30) Priority Data:</b> 9624840.6 29 November 1996 (29.11.96) GB  <b>(71) Applicant (for AU BB CA GR GH IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only):</b> UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).  <b>(71) Applicant (for all designated States except AU BB CA GB GH IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG US ZW):</b> UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).  <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> THOMPSON, Katherine, Mary [GB/GB]; 19 Ambleside Close, Thingwall, Wirral, Merseyside L61 3XG (GB). THORNTHWAITE, David, William [GB/GB]; Lorient, 23 Leighton Road, Neston, South Wirral, Cheshire L64 3SF (GB).		<b>(74) Agent:</b> ELLIOTT, Peter, William; Unilever plc, Patent Division, Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).  <b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>Without international search report and to be republished upon receipt of that report.</i>
<b>(54) Title:</b> IMPROVEMENTS RELATING TO BLEACHING COMPOSITIONS COMPRISING HYDROGEN PEROXIDE  <b>(57) Abstract</b> <p>The invention provides a bleaching composition of pH 10-14 which comprises an oxygen transfer agent and hydrogen peroxide. It is believed that the reaction of hydrogen peroxide with the imine quat. oxygen transfer agents proceeds through a different route than that of the organic and inorganic peroxides. As a consequence, the formation of acyl hydroxamate is significantly reduced. Furthermore it is believed that when hydrogen peroxide is used as the bleaching agent in the pH range indicated, a surprising improvement in the efficacy of the bleaching system occurs and it is possible to formulate peroxide based systems which have efficacy approaching or exceeding that of hypochlorite without the disadvantages associated with hypochlorite. A further aspect of the present invention provides a method for bleaching a stained substrate which comprises the step of treating the substrate with a bleaching composition of pH 10-14, which bleaching composition comprises an oxygen transfer agent and hydrogen peroxide.</p>		

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IMPROVEMENTS RELATING TO BLEACHING COMPOSITIONS  
COMPRISING HYDROGEN PEROXIDE

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Field of the Invention

The present invention relates to bleaching compositions comprising hydrogen peroxide.

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Background to the Invention

In household cleaning, fabric washing and in many  
15 other areas there is a general need for agents which  
can 'bleach' unsightly materials, i.e. which can react  
with these materials to decolourise them. One of the  
commonest of such bleaching agents is sodium  
hypochlorite, which is widely used in cleaning  
20 compositions to decolourise soils, to assist in  
cleaning through its reaction with soils and to kill  
micro-organisms.

Sodium hypochlorite is a powerful oxidising agent,  
25 which can decolourise a very large number of coloured  
compounds found in soils but which has significant  
limitations when used to bleach certain fatty and  
pyrolised soils. Many consumers prefer not to use  
chlorine-based bleach compounds due the characteristic  
30 and pungent smell of chlorine. In some circumstances  
the use of a chlorine containing bleaching composition  
must be avoided due to the possibly adverse effects of  
mixing such compositions with acidic bathroom cleaners  
and the resulting release of chlorine gas.

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There is a need for an alternative to chlorine-based bleaching and bleaching/cleaning agents. One well known class of alternatives are the peroxygen compounds. While these have been used extensively as bleaching and cleaning agents, the efficacy of peroxygen compounds as bleaching agents falls short of that of hypochlorite. There is therefore a general need to find new alternatives to chlorine based bleaching agents and to improve the properties of these towards that of hypochlorite.

It is known to use oxygen transfer agents such as 'imine quat' compounds to promote the bleaching activity of peroxygen compounds. In the context of the present invention, an oxygen transfer agent is a species which reacts with a peroxygen compound such as hydrogen peroxide to form an oxidative bleaching species which oxidative bleaching species, subsequently reacts with a substrate to regenerate the oxygen transfer agent.

Such oxygen transfer agents include N-methyl-3,4-dihydroisoquinolinium salts. US 5360569 discloses that imine quat molecules can be used to promote the activity of TAED/perborate bleaching compositions. These systems are believed to work by generating peracetic acid in situ. This organic peroxide is believed to interact with the imine quat. to bring about the bleaching activity. US 5360568 discloses that imine quat molecules can be used to promote the activity of monopersulphate (an inorganic peroxygen compound) and peroxy-adipyl-phthalimide (PAP) (an the organic peracid).

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In the above-mentioned compositions the imine quat is believed to be converted, by reaction with the peracid into an oxaziradinium salt which can act as an oxygen donor (i.e. a bleaching species) and which is

5 converted back into the imine quat. The oxaziradinium ion is however unstable at high pH in the compositions described above, where it is believed to be converted into an acyl hydroxamate thereby preventing the bleaching cycle from working efficiently. As a

10 result, compositions have been limited in pH range and it has proved difficult to formulate compositions which are effective against the more recalcitrant stains particularly hydrophobic and/or pyrolised stains.

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#### Brief Description of the Invention

It is believed that the above-mentioned problem is

20 overcome by the use of hydrogen peroxide, rather than an organic peracid or an inorganic peroxide, as the source of oxidising equivalents. This enables the formulation of compositions to bleach at relatively high pH's where some of the more difficult stains are

25 soluble and hence accessible to the formulation. Other, hitherto unsuspected benefits arise from the use of hydrogen peroxide as are described below.

Accordingly, the present invention provides a

30 bleaching composition of pH 10-14 which comprises an oxygen transfer agent and hydrogen peroxide.

Without wishing to limit the scope of the present specification by reference to some theory of

35 operation, it is believed that the reaction of

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hydrogen peroxide with the imine quat. oxygen transfer agents proceeds through a different route than that of the organic and inorganic peroxides mentioned above. As a consequence, the formation of acyl hydroxamate is significantly reduced. Furthermore it is believed that when hydrogen peroxide is used as the bleaching agent in the pH range indicated, a surprising improvement in the efficacy of the bleaching system occurs and it is possible to formulate peroxide based systems which have efficacy approaching or exceeding that of hypochlorite without the disadvantages associated with hypochlorite.

A further aspect of the present invention provides a method for bleaching a stained substrate which comprises the step of treating the substrate with a bleaching composition of pH 10-14 which bleaching composition comprises an oxygen transfer agent and hydrogen peroxide.

#### Detailed Description of the Invention

As noted above, hydrogen peroxide is an essential component of the compositions according to the present invention. As hydrogen peroxide is a reactive species, this will place some limitations on the other components which can be present. These are described in greater detail below.

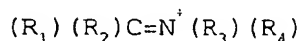
Hydrogen peroxide is preferably present at a level of 0.5-10%wt on product, more preferably 1-5%wt on product. In typical embodiments of the invention the weight ratio of the hydrogen peroxide to the oxygen transfer agent falls in the range 5:1 to 20:1.

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Oxygen Transfer Agents

Oxygen transfer agents for use in the present invention, include, but are not limited to, the imine quat. N-methyl-3,4-dihydroisoquinolinium salts. Where these salts are used, suitable counter-ions include halides, sulphate, methosulphate, sulphonate, p-toluene sulphonate and phosphate. Oxygen transfer agents which comprise a quaternary nitrogen atom are preferred.

A broad class of oxygen transfer agents suitable for use in embodiments of the present invention are compounds comprising ions of the general structure:



Wherein:

$R_1$  and  $R_4$  are in a *cis*- relation and are substituted or unsubstituted moieties selected from the group consisting of hydrogen, phenyl, aryl, heterocyclic ring, alkyl and cycloalkyl radicals:

$R_2$  is a substituted or unsubstituted moiety selected from the group consisting of hydrogen, phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nito, halo, cyano, alkoxy, keto, carboxylic acid and carboalkoxy groups:

$R_3$  is a substituted or unsubstituted moiety selected from the group consisting of hydrogen, phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nito, halo and cyano groups:

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Preferably,  $R_1$  with  $R_2$  and  $R_3$  respectively together form a moiety selected from the group consisting of cycloalkyl, polycyclo, heterocyclic and aromatic ring systems.

5

Heterocyclic rings according to the present specification include cycloaliphatic and cycloaromatic type radicals incorporating an oxygen, sulphur and/or nitrogen atom within the ring system. Representative nitrogen heterocycles include pyridine, pyrrole, imidazole, triazole, tetrazole, morpholine, pyrrolidone,

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piperidine and piperazine. Suitable oxygen heterocycles include furan, tetrahydrofuran and dioxane.

Sulphur heterocycles may include thiophene and

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tetrahydrothiophene.

The term substituted as used in relation to  $R_1$ ,  $R_2$ ,  $R_3$

and  $R_4$  includes a substituent which is nitro, halo,

cyano, C1-C20 alkyl, amino, aminoalkyl, thioalkyl,

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sulphoalkyl, carboxyester, hydroxy, C1-C20 alkoxy, polyalkoxy, or C1-C40 quaternary di- or tri-alkyl ammonium.

Preferred oxygen transfer agents are quaternary imine

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salts, particularly those set forth in US patent specification 5,360,568 (Madison and Coope), more particularly the substituted or unsubstituted

isoquinolinium salts, preferably the 3,4 di-hydro

isoquinolinium salts and more preferably the N-methyl

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3,4 di-hydro-isoquinolinium salts. N-methyl 3,4 di-hydro-isoquinolinium p-toluene sulphonate is a particularly preferred oxygen transfer agent.

Typically, the oxygen transfer agents are present of

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levels of 0.001-10%wt on product. Preferably, the



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oxygen transfer agents are present at levels of 0.01-1%wt on product, more preferably 0.1-0.5%wt on product.

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### Surfactants

It is preferred that the compositions according to the invention further comprise one or more surfactant species. Surfactants can be nonionic, anionic, cationic, amphoteric or zwitterionic provided that they, and where appropriate their counter-ions, do not react substantially with the oxygen transfer agent or the hydrogen peroxide.

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Suitable nonionic detergent active compounds can be broadly described as compounds produced by the condensation of alkylene oxide groups, which are hydrophilic in nature, with an organic hydrophobic compound which may be aliphatic or alkyl aromatic in nature. The length of the hydrophilic or polyoxyalkylene radical which is condensed with any particular hydrophobic group can be readily adjusted to yield a water-soluble compound having the desired degree of balance between hydrophilic and hydrophobic elements.

Particular examples include the condensation product of aliphatic alcohols having from 8 to 22 carbon atoms in either straight or branched chain configuration with ethylene oxide, such as a coconut oil ethylene oxide condensate having from 3 to 10 moles of ethylene oxide per mole of coconut alcohol; condensates of alkylphenols whose alkyl group contains from 6 to 12

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carbon atoms with 3 to 10 moles of ethylene oxide per mole of alkylphenol.

5 The preferred alkoxyated alcohol nonionic surfactants are ethoxylated alcohols having a chain length of C9-C11 and an EO value of at least 3 but less than 10. Particularly preferred nonionic surfactants include the condensation products of C<sub>10</sub> alcohols with 3-8 moles of ethylene oxide. The preferred ethoxylated  
10 alcohols have a calculated HLB of 10-16. An example of a suitable surfactant is 'IMBENTIN 91-35 OFA' (TM, ex. Kolb AG) a C<sub>9-11</sub> alcohol with five moles of ethoxylation.

15 Alternative surfactants include amine oxides, amines and/or ethoxylates thereof. Amine oxides with a carbon chain length of C12-C14 are particularly preferred.

20 When present, the amount of nonionic detergent active to be employed in the composition of the invention will generally be from 0.01 to 30%wt, preferably from 0.1 to 20%wt, and most preferably from 3 to 10%wt for non-concentrated products. Concentrated products will  
25 have 10-20%wt nonionic surfactant present, whereas dilute products suitable for spraying will have 0.1-5%wt nonionic surfactant present.

#### pH

30 As noted above the pH of compositions according to the present invention falls in the range 10-14. pH of compositions is preferably 10-12, more preferably 10-11. At these higher pH's we have found that the  
35 composition penetrates more readily into the soils.

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As is noted in the illustrative examples given below, the use of oxygen transfer agents at high pH is contra-indicated by their tendency to increase the colour of a stain rather than reduce it.

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### Minors

Minor components of compositions according to the present invention include those typically present in cleaning compositions.

In compositions which contain hydrogen peroxide it is useful to include a metal ion complexing agent to retard decomposition of the peroxide by any metal ions which may be present as contaminants or such as are introduced during processing. Again, these components should be selected such that they do not react do not react substantially with the oxygen transfer agent or the hydrogen peroxide.

Preferably, cleaning and/or disinfecting compositions according to the invention will further comprise metal ion sequestrants such as ethylene-diamine-tetra-acetates, amino-polyphosphonates (such as those in the DEQUEST (TM) range) and phosphates and a wide variety of other poly-functional organic acids and salts, can also optionally be employed. Preferred metal ion sequesterants are selected from dipicolinic acid, ethylene diamine tetra acetic acid (EDTA) and its salts, hydroxy-ethylidene diphosphonic acid (Dequest 2010, RTM), ethylene diamine tetra (methylene phosphonic acid) (Dequest 2040, RTM), diethylene triamine penta(methylene phosphonic acid) (Dequest 2060, RTM), amino tri(methylene phosphonic acid)

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(Dequest 2000, RTM). The phosphonic acid derivatives are particularly preferred. It is preferred that the level of phosphonic acid derivative metal ion complexing agent should fall into the range 0.05-5%.

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Preferably, cleaning and/or disinfecting compositions according to the invention will further comprise at least 1% of a solvent of the form  $R_1-O-(EO)_m-(PO)_n-R_2$ , wherein  $R_1$  and  $R_2$  are independently C2-6 alkyl or H,

10 but not both hydrogen, m and n are independently 0-5. More preferably, the solvent is selected from the group comprising di-ethylene glycol mono n-butyl ether, mono-ethylene glycol mono n-butyl ether, propylene glycol n-butyl ether, isopropanol, ethanol, 15 butanol and mixtures thereof. Typically, the level of solvent in cleaning and disinfecting compositions is 1-10%, with a solvent: nonionic ratio of 1:3-3:1 being particularly preferred.

20 Where compositions according to the present invention are liquids, they can be water-thin or thickened. Thickened compositions are advantageous in that they cling to sloping surfaces and find particular utility in toilet cleaners. Slight thickening of the 25 composition is desirable for applications in which the composition is sprayed, so as to reduce the extent to which small droplets are produced which might otherwise cause respiratory irritation to the user. Suitable thickening agents include amine oxide and 30 soap and systems based on nonionic surfactants.

Compositions according to the invention can also contain, in addition to the ingredients already mentioned, various other optional ingredients such as, 35 colourants, optical brighteners, soil suspending

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agents, deterative enzymes, gel-control agents, freeze-thaw stabilisers, further bactericides, perfumes and opacifiers .

- 5 A particularly preferred compositions according to the present invention comprises a bleaching composition having a pH of 10-12, said composition being an aqueous liquid and comprising:
- 10 a) hydrogen peroxide at a level of 0.5-10%wt on product,
- b) 0.001-10%wt on product of an isoquinolinium salt,
- 15 c) 0.01 to 30%wt on product of at least one nonionic surfactant, and,
- d) optional minors selected from the group consisting of metal ion sequestering agents,
- 20 solvents and perfumes.

#### Product form

- 25 Products according to the present invention are generally liquids and preferably aqueous. However, other product forms including pastes and solids are also envisaged.
- 30 As will be appreciated, the product form is largely determined by the end use and consequently liquids are generally suitable for use as hard surface cleaners, including cleaners for industrial, institutional and domestic cleaning and/or disinfection of hard surfaces

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including metal, plastics materials or other polymers, ceramic, and glass surfaces.

It is envisaged the method of the present invention  
5 can be applied in the cleaning of surfaces used for  
the preparation of food and beverages (e.g. worktops,  
conveyor systems and utensils) or other industrial,  
institutional and domestic surfaces such as sanitary  
ware, industrial, institutional and domestic fluid  
10 supply applications, for disinfection of medical,  
surgical or dental apparatus, equipment, facilities or  
supplies, catheters, contact lens', surgical dressings  
or surgical instruments, in horticultural  
applications, e.g. for sterilising the surfaces of  
15 greenhouses, for soft surfaces including fabrics  
(including in dressings, wipes and cloths), and non-  
living materials of biological origin (such as wood).  
Solid product forms are suitable for use as toilet and  
urinal blocks and other uses where slow or delayed  
20 release of the components is required.

In order that the present invention may be further  
understood it will be described hereinafter by  
reference to illustrative and non-limiting examples  
25 and comparisons.

#### EXAMPLES

30 The following examples were performed using model  
kitchen soils and a soiling procedure as described  
below. The soils were chosen to have recalcitrant  
stains, which would be difficult to bleach due to the  
hydrophobic or pyrolised nature of the stain.

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Example 1: Curcumin/oil stain on formica (TM).Soil preparation

- 5 Flat tiles, measuring 4" x 4", are cut from white Formica sheeting and their surfaces thoroughly cleaned using a commercially available liquid abrasive cleaner, 'Jif' (TM). After rinsing with demineralised water, the tiles are allowed to dry at room  
10 temperature.

- The curcumin/oil stain is prepared by mixing 19 g of vegetable oil and 180 g of ethanol and then adding 1 g of pure curcumin (a pigment found in curry powder).  
15 After thorough stirring, the resulting solution is sprayed onto the tiles using an airbrush propellant canister so as to give a uniform surface coverage. The tiles are left to dry for a minimum of 10 minutes, during which time the ethanol evaporates leaving a  
20 bright yellow, slightly sticky, oily stain, which cannot be removed by wiping or rinsing with water. Curcumin is susceptible to photo-oxidation and stained tiles should not be stored for periods exceeding 2 hours before use.

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Preparation of Bleach or Surfactant Solutions

- Experiments were performed with hydrogen peroxide, PAP  
30 (peroxy-adipoyl-phthalimide), peroxymonosulphate and sodium hypochlorite (a well known inorganic bleaching agent).

- Bleach solutions are prepared by dissolving the  
35 peroxide co-oxidant in demineralised water and, where

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necessary, adding the oxygen transfer agent. Sodium hydroxide solution ( $5 \text{ mol dm}^{-3}$ ) is added dropwise to adjust the pH to the desired value, as determined using a pH meter. Further demineralised water is added to the solution to give the desired final volume.

In the examples described the oxygen transfer agent was N-methyl 3,4 di-hydro isoquinolinium p-toluene sulphonate. The preparation of this material is described in US 5360569 and US 5360568 which are incorporated herein by reference. The material is referred to below as the 'Imine Quat'.

Hydrogen peroxide solutions are prepared to achieve a final concentration of 3 w/w % ( $0.88 \text{ mol dm}^{-3}$ ) and used in conjunction with a 1% molar equivalency of the Imine Quat catalyst ( $0.0088 \text{ mol dm}^{-3}$ , 0.30 w/w %). Solutions of potassium Caroate (TM: 6 w/w%, equivalent to 3 w/w%,  $0.2 \text{ mol dm}^{-3}$  peroxomonosulphate) and PAP (6-[N-phthalimido]-perhexanoic acid: 2 w/w%,  $0.012 \text{ mol dm}^{-3}$ ) were examined in combination with the same level of Imine Quat. The potassium peroxymonosulphate system was examined at pH 8.5 (but higher pH values were used for hydrogen peroxide (which has a higher  $\text{pK}_a$ ) and PAP (which is relatively insoluble at lower alkalinities). Addition of a wetting agent (1% butyl digol (TM): diethylene glycol mono n-butyl ether) further increases the PAP solubility.

The bleach systems are compared with the detergency obtained using a  $\text{C}_{9-11} \text{EO}_5$  nonionic surfactant, Imbentin 91-35 OFA (TM) in the formulations listed in TABLE 1 below. In some instances a solvent 'Butyl Digol'



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(TM), di-ethylene glycol mono-n-butyl ether, was added or used for comparison.

5 Soil removal experiments

Examples were performed at room temperature. A glass ring, of diameter 50 mm and height 15 mm, is placed over the centre of the stained tile and 5 cm<sup>3</sup> of the aqueous bleach or surfactant solution is pipetted within the annulus of the ring. The solution is allowed to remain in contact with the stained tile surface for 30 seconds, after which the glass ring is removed and the solution poured away. The tile is immediately rinsed with demineralised water for a further 30 seconds and then allowed to dry. Each solution is used to treat two tiles.

The extent of stain removal is assessed visually by a panel of at least 15 people, using a standard scale. Tiles are graded on an integer scale ranging from 0 to 5, where 0 denotes no visible soil removal and 5 corresponds to total removal. A minimum of two stained tiles are treated with each bleach solution and mean scores for each system are calculated by averaging the scores from both tiles.

Results are shown in TABLE 1 below. From the results presented in TABLE 1, it can be seen that a significant improvement as regards hydrogen peroxide bleaching is obtained in the presence of the Imine Quat at both pH 10 and pH 10.5. A similar increase is not seen for either the organic or inorganic peroxy acid.

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Comparing the results with conventional cleaning/bleaching systems. It can be seen that use of an oxygen transfer agent together with hydrogen peroxide provides results which are very favourably  
5 comparable with hypochlorite, and significantly better than alkali and surfactant based systems.

TABLE 1

System	Without Imine Quat.	With 0.3% Imine Quat
3% Hydrogen Peroxide at pH 10.0	0.1	1.3
3% Hydrogen Peroxide at pH 10.5	1.3	3.1
2% PAP/1% Butyl Digol at pH 10.0	0.1	0.3
3% K-monoperoxysulphate at pH 8.5	0	0
1% NaOCl at pH 10	2.9	-
1% NaOCl at pH 10.5	3.8	-
Alkali at pH 10.0	0.2	-
Alkali at pH 10.5	1.6	colour of stain increased
0.1% Imbentin at pH 10.0	1.0	-
0.1% Imbentin at pH 10.5	1.5	-

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Example 2: Baked fat/flour on enamelSoil preparation

- 5 Oleic acid (1 g), stearic acid (1 g) and Friol (TM)  
Italian Oil (38 g) are mixed in a metal beaker and  
directly heated, using a hotplate, to a temperature of  
60°C, so that the mixture liquifies. Demineralised  
water (100 g) is boiled and allowed to cool to 60°C  
10 before mixing with Italian flour (40 g) to make a  
thick paste.

- The organic acid-oil mixture and the flour paste are  
placed in a liquidiser jug and demineralised water  
15 (280 g) added. The fat-flour mixture is blended for 5  
seconds, allowed to stand for 10 seconds and then  
blended for a further 5 seconds. The contents of the  
liquidiser are then transferred to a glass beaker and  
gently warmed by direct heating over a hot-plate. The  
20 mixture is allowed to simmer for five minutes with  
constant agitation from an overhead stirrer. The  
mixture must not be allowed to stick to the beaker or  
excessive cross-linking will occur, resulting in a  
soil that is overly resistant to removal. The mix is  
25 then transferred to a polythene beaker and allowed to  
cool before use.

Soil application

- 30 White enamel tiles (100 mm x 100 mm) are cleaned using  
a commercially available liquid abrasive cleaner  
(*'Jif'* (TM)), rinsed in demineralised water and  
allowed to dry. The tiles are then coated with a thin  
35 (c.a. 0.5 mm) layer of the fat/flour mix using a

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screen printing technique. A flexible rubber paddle is used to spread the mix onto the tile surface, through a thin plastic mesh, taking care to achieve a uniformly thin coverage. The soiled tiles are allowed  
5 to stand overnight in the open air, acquiring a uniform matt finish. The tiles are baked on the middle shelf of an oven at 190°C for one hour, developing a light brown colouration, and allowed to cool for 2 hours before cleaning. As there is  
10 expected to be variation between batches of these tiles soiled and subsequently pyrolised, it is important that comparisons are performed with tiles taken from the same batch.

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#### Preparation of Bleach and Surfactant Solutions

Solutions are prepared as described for the curcumin-oil soil removal experiments described above with  
20 reference to TABLE 1 using the formulations listed in TABLE 2 below. Detergency effects have been studied using Neodol 91-5 (TM) nonionic surfactant, a commercially available, slightly less pure, version of the Imbentin 91-35 OFA (TM) surfactant used in the  
25 curcumin/oil experiments above. Admox 10 (TM) is a C<sub>10</sub> amine oxide surfactant.

Peracetic acid is used at a concentration equal to that of the HOO<sup>-</sup> active oxidising species present in  
30 the 3% hydrogen peroxide solution at the same pH (10.0).

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Soil removal experiments

Soil removal is carried out using a standard Wool Industries Research Association Abrasion Tester (WIRA: 5 TM) apparatus. Two soiled tiles are cleaned simultaneously with the same solution, to provide duplicate results. The bleach or surfactant solution (20 cm<sup>3</sup>) is poured onto the surface of the tile, and 10 rubbed using a cleaning head covered with two layers of clean 'J'-cloth (TM) material. Each tile is cleaned using 51 strokes of the head. The tiles are then immediately removed from the apparatus, rinsed under running water and patted dry using paper tissues.

15 As noted above, although the colouration and ease of soil removal is uniform for tiles coated with a specific fat-flour mixture, there is some variability between different batches of soil. Consequently, the 20 results shown below in TABLE 2 are grouped in sets (TABLE 2a, 2b and 2c), each carried out using a different batch of fat-flour soiled tiles. Experiments using Jif (TM) liquid abrasive cleaner and Domestos Multi-Surface Cleaner (TM), a commercial 25 hypochlorite hard surface cleaning product, are included in each series of runs to provide reference standards. The extent of soil removal is assessed visually by a panel of at least 5 people, using a standard scale. Tiles are graded on a scale ranging 30 from 0 to 10, and panellists award integer or half-integer scores to each tile. A score of 0 denotes no visible soil removal and 10 corresponds to total soil removal. Mean scores for each soil removal system are calculated by averaging scores from both replicates.

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Comparing the results with conventional cleaning/bleaching systems, it can be seen that use of an oxygen transfer agent together with hydrogen peroxide provides results which are very favourably comparable with hypochlorite and commercial products based on hypochlorite, and which are significantly better than alkali and surfactant based systems. It can be seen from table 2d that while the imine quat shows a reduced effect in the presence of surfactant, the improvement over systems which do not contain the imine quat. is still measurable.

TABLE 2a

System	Without Imine Quat.	With 0.3% Imine Quat
3% Hydrogen Peroxide at pH 10.5	8.5	9.0
3% K-monoperoxysulphate at pH 8.5	5.6	5.6
Domestos Multi Surface Cleaner at pH 11.5	10	-
JIF at pH 11.0	5.8	-
Alkali at pH 10.5	6.4	-
0.1% Neodol at pH 10.5	3.5	-

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TABLE 2b

System	Without Imine Quat.	With 0.3% Imine Quat.
3% Hydrogen Peroxide at pH 10.0	3.9	4.9
0.12% peracetic acid at pH 10.0	2.9	3.8
Domestos Multi Surface Cleaner at pH 11.5	9.1	-
JIF at pH 11.0	3.6	-

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TABLE 2c

System	Without Imine Quat.	With 0.3% Imine Quat
3% Hydrogen Peroxide at pH 10.0	7.2	9.1
Domestos Multi Surface Cleaner at pH 11.5	10	-
3% NaOCl at pH 10.0	8.1	-



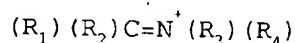
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TABLE 2d

System	Without Imine Quat.	With 0.3% Imine Quat
3% Hydrogen Peroxide at pH 10.0	7.5	8.0
3% Hydrogen Peroxide & 0.1% Admox 10 at pH 10.0	7.3	7.9
Domestos Multi Surface Cleaner at pH 11.5	9.4	-
JIF at pH 11.0	4.3	-

CLAIMS

- 5 1. A bleaching composition of pH 10-14 which  
comprises an oxygen transfer agent and hydrogen  
peroxide.
- 10 2. A bleaching composition according to claim 1  
wherein hydrogen peroxide is present at a level  
of 0.5-10%wt on product.
- 15 3. A bleaching composition according to claim 1  
wherein the weight ratio of the hydrogen peroxide  
to the oxygen transfer agent falls in the range  
5:1 to 20:1.
- 20 4. A bleaching composition according to claim 1  
wherein the oxygen transfer agent is a compound  
comprising ions of the general structure:



wherein:

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$R_1$  and  $R_4$  are in a *cis*- relation and are  
substituted or unsubstituted radicals selected  
from the group consisting of hydrogen, phenyl,  
aryl, heterocyclic ring, alkyl and cycloalkyl  
30 radicals:

$R_2$  is a substituted or unsubstituted radical  
selected from the group consisting of hydrogen,  
phenyl, aryl, heterocyclic ring, alkyl,

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cycloalkyl, nito, halo, cyano, alkoxy, keto, carboxylic acid and carboalkoxy groups; and,

$R_3$  is a substituted or unsubstituted radical selected from the group consisting of hydrogen, phenyl, aryl, heterocyclic ring, alkyl, cycloalkyl, nito, halo and cyano groups:

- 5                    5.    A bleaching composition according to claim 4  
10                   wherein the oxygen transfer agent is a  
                     substituted or unsubstituted isoquinolinium salt.
6.    A bleaching composition according to claim 1  
15                   having a pH of 10-12, said composition being an  
                     aqueous liquid and comprising:
- a)    hydrogen peroxide at a level of 0.5-10%wt on  
                             product,
- 20                   b)    0.001-10%wt on product of an isoquinolinium  
                             salt,
- c)    0.01 to 30%wt on product of at least one  
                             nonionic surfactant, and,
- 25                   d)    optional minors selected from the group  
                             consisting of metal ion sequestering agents,  
                             solvents and perfumes.
- 30    7.    A method for bleaching a stained substrate which  
                 comprises the step of treating the substrate with  
                 a bleaching composition as defined in any one of  
                 claims 1-6.

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